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ORIGINAL PAPER

Modeling of Wheat Straw Torrefaction as a Preliminary Tool for Process Design

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Abstract Torrefaction is considered as a kind of mild pyrolysis that is carried out under inert atmosphere (usually nitrogen) conditions. During this process, the moisture of the initial fuel and a portion of its volatiles are removed from the biomass particles towards the inert atmosphere. The resulted torrefied solid biomass has high energy density, durability and less hydrophilic character. The most beneficial result of torrefaction process is that biomass feedstock logistics cost can be reduced, as less tones of biomass are required for a given amount of energy input. The development of a process model examining basic parameters as reaction temperature and residence time can provide useful information, which can be used for the more efficient design of a torrefaction reactor. This study presents such a process model for a straw torrefaction pilot plant. This model is based on the thermodynamic calculation of a single and/or a two batch reactor, built on the commercial software ASPEN Plus. The calculation of required flow rates of inert gas, cooling medium for a specific biomass feedstock value, is based on relevant results found in literature.

Keywords Wheat straw · Torrefaction · Thermodynamic modeling · ASPEN Plus

List of symbols

C_p	Heat capacity coefficient (J/kg K)
E	Activation energy (J/mol K)
M	Mass yield (kg)
K	Kinetic rate (1/s)
t	Time (s)
t_{heat}	Heating time required for achievement of torrefaction temperature (s)
t*	Critical time at which the second stage of torrefaction begins and dominates over the first one (s)

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T	Temperature (K or °C)
W	Solid residual mass at each time step (kg)

Greek letters

λ	Thermal conductivity (W/m K)
ρ	Density (kg/m^3)

Abbreviations

CV	Calorific value (MJ/kg)
ER	Energy recovery (-)
HHV	High heating value (MJ/kg)
LHV	Low heating value (MJ/kg)

Subscripts

0	Initial properties of biomass at $t = 0$ s
A	Biomass properties during the first stage of torrefaction
B	The intermediate reaction solid product properties
C	The final torrefied biomass properties
V1	Properties of volatiles as produced during the first phase
V2	Properties of volatiles as produced during the second phase
raw	Raw materials properties
tor	Torrefaction material properties
1	Stage 1
2	Stage 2

Introduction

Nowadays, the efforts for the achievement of high calorific value alternative biogenic fuels, are intensified. Torrefaction is a thermal pre-treatment technique applicable for biomass conversion into energy and heat by combustion, gasification or co-firing with conventional solid fuels. The torrefaction treatment not only decomposes the fibrous structure and tenacity of biomass, but it as well increases its calorific value. Additionally, after the torrefaction the biomass obtains less hydrophilic characteristics, thus allowing the higher time storage of torrefied biomass, because of its rotting behavior. Specifically, due to the breakage of OH-groups in torrefaction process, the material losses its tendency to absorb water so it remains more stable and hydrophobic [1] compared to the raw fuel. Specifically for straw, because of its abundance and low moisture, in comparison with other types of biomass (wood), this is considered as a very promising fuel in which torrefaction can be applied.

In general, the major advantage of using torrefied pelletized biomass instead of raw biomass is the considerable reduction of the CO_2 footprint associated with its transport and its co-combustion with conventional solid fuels. Moreover, torrefied biomass has properties which resemble more those of conventional solid fuels H/C and O/C ratios) compared to raw one. These facts have a considerable added value for the energy utilization of torrefied biogenic fuels in comparison with their raw form, as the biomass fuel transportation cost is reducing for the same energy gain, its heating value is increasing, while the cost of modifications that should be made in small and/or large scale power plants when co-firing scenarios are applied, is decreasing. From an operational point of view, the moisture content of torrefied pellets much less than the corresponding of raw one and therefore the amount of heat required to be provided by other energy sources for their final energy utilization (i.e. pyrolysis, gasification, combustion) is much less than that the one required for the raw one.

On the other hand, the installation and operational cost of the torrefaction plant increase the overall investment cost of a power producer. However, for one to make a more accurate estimation of the advantages and disadvantages of this process, a LCA (Life Cycle Assessment) and a CBA (Cost Benefit Analysis) analysis should be in depth made.

Torrefaction is a mild pyrolysis process carried out at temperatures 200–300 °C, in which three basic components are produced including, (a) a solid product of a brown/dark color, (b) a condensable liquid including mostly water, acetic acid, and other oxygenates and (c) non condensable gases—mainly CO_2, CO, and small amounts of CH_4 and H_2. Their yield depends upon the (a) reaction temperature, (b) the residence time and (c) the raw material biomass properties.

The solid phase consists of a chaotic structure of sugars and other reaction substances. The content of carbon in the solid product increases, the higher the torrefaction temperature and the longer the residence time are. The increase of the torrefied biomass calorific value is owed to the decrease of hydrogen and oxygen [2, 3]. The gas phase includes main gases, such as CO, CO_2 and CH_4, but as well light aromatic components such as benzene and toluene, but with very small concentration (traces) [4]. According to Ferro et al. [2] and Wang et al. [5] the content of CH_4, H_2, C_xH_y and CO in the product gases increases as the torrefaction temperature increases, while the content of CO_2 decreases. The condensable part or liquids comprises mainly of water, organics and lipids. Water content can reach up to a high percent, as this is released from the biomass during its evaporation phase. The organics subgroup (in liquid form) comprises of compounds mainly produced during devolatilization and carbonization. Finally, the lipids subgroup contains compounds such as waxes and fatty acids that are present in the original biomass. According to Wang et al. [5], the yield of liquid products increases as the temperature increases because of the decomposition of hemicellulose.

Torrefaction has a great influence on the physical/chemical properties of the solid product, mainly caused by the removal of oxygen from the original solid biomass resource. In this way, the net calorific value is increasing and the product becomes more energy dense. According to Shang et al. [6], the percent of energy loss increases faster than the weight loss, with the torrefaction conditions getting more severe. This happens because of the degradation of lignin and cellulose in the temperature range of 270–300 °C. So in order to achieve the most desired energy content in the torrefied material, special attention should be paid on the parameters of temperature and residence time, during this complicated process.

In this frame, an important parameter influencing significantly the characteristics of the solid yield, is the raw material composition (in this case study: straw pellets), in terms of hemicellulose, cellulose and lignin content. Straw pellets consist of around 7.7 % lignin 41.3 % cellulose and 30.8 % hemicellulose [3]. The composition is given in dry ash free basis. Hence, the total dry matter digestibility (DMD) of straw pellets is equal to 79.8 %. The rest of the composition includes other materials such as resin. Hemicellulose is the most reactive among the three lignocelluloses components found in biomass and during torrefaction it undergoes the most significant decomposition reactions. According to Peng et al. [7], hemicelluloses isolated from dignified wheat straw are consisting of arabinoxylan and uronic acids, which have the typical structure of straw hemicelluloses. Such typical monomers are glucose, xylose, galactose, arabinose, glucuronic and galacturonic acids. The TG and DTG curves from the Peng et al. [7] suggest that decomposition of hemicellulose mainly happens in the range from 190 to 350 °C. The corresponding temperature of cellulose decomposition is in-between 305 °C and 375 °C, whilst lignin gradually decomposes over a temperature range of 250–500 °C. It is mentioned that studies conducted using xylan (the prominent hemicellulose found in herbaceous biomass) have concluded that decomposition of hemicellulose initiates at temperatures above 200 °C, while full devolatilization occurs by 400 °C.

Table 1 presents a short description of all the experimental investigations for straw torrefaction, found in the literature. Some of them are carried out in various types of reactors and other using the TGA equipment. The parameters influencing the torrefaction process include the straw and nitrogen mass flow rates, the heating rate, the operating torrefaction temperature and finally the residence time. The studies summarized in this Table are conducted by Bridgman et al. [3], Lanzetta and Blasi [8], Prins et al. [9], Ferro et al. [2], Wang et al. [5] and Sadaka et al. [10]. The experimental results from the aforementioned studies conclude that the higher the torrefaction temperature is, the lower the quality yield of charcoal is, while the energy density increases and the energy yield decreases. The apparent volume of the solid products decreases significantly and their grind ability improves greatly with an increase in temperature.

For quite high temperatures (above 247 °C), two consecutive reactions describe the temporal evolution of weight loss. In the first phase, raw biomass particles break into volatile gases and an intermediate solid compound, which in turn break again into volatiles and a solid residual (second phase), often named as char residual.

The scope of this paper is the definition of a set of design parameters for a pilot scale straw pellets torrefaction reactor, of a capacity equal to around capacity 100 kg/h. For this scope, a thermodynamic tool describing the torrefaction process is built in the ASPEN Plus commercial package. Very few simulation tools for this process can be found in the recent literature, [11, 12]. A parametric study on the effect of residence time and temperature on the final properties of the torrefied biomass for a given raw biomass flow rate is conducted. Among all the derived results, the conditions reflecting the most efficient operation of the pilot plant are selected for its further design, drawing and manufacturing can be derived.

Set up of the Thermodynamic Model

Products Yield

The prediction of weight loss of the biomass feedstock is based on the two-stage mechanism, first introduced by Di Blasi and Lanzetta [8], [13]. According to it, for an operating torrefaction temperature above 250 °C, torrefaction is conducted in two consecutive stages, as depicted in Fig. 1.

In this Figure, subscript A denotes the raw biomass, B the intermediate reaction solid product, C the final torrefied biomass and V_1, V_2 the volatiles, as produced during the first and second phases respectively. In fact, the first stage represents the degradation of hemicellulose, whereas the second one the degradation of lignin. The differential equations that express the mass loss or production for a constant temperature along with time for stage 1 are:

$$\frac{dM_A}{dt} = -K_1 M_A \Rightarrow M_A = M_0 e^{-K_1 t} \tag{1a}$$

$$\frac{dM_{V1}}{dt} = K_{V1} M_A \Rightarrow M_{V1} = \frac{K_{V1}}{K_1} M_0 \left(1 - e^{-K_1 t}\right) \tag{1b}$$

$$\frac{dM_B^{A\to B}}{dt} = K_B M_A \Rightarrow M_B^{A\to B} = \frac{K_B}{K_1} M_0 \left(1 - e^{-K_1 t}\right) \tag{1c}$$

where M_0 is the initial mass of biomass and $M_B^{A\to B}$is the mass of B as produced from the mass of A (M_A), at each time step. The corresponding kinetic rates for each stage (1 and 2) are expressed as:

$$K_1 = K_B + K_{V1} \tag{2a}$$

$$K_2 = K_C + K_{V2} \tag{2b}$$

Table 1 Summary of experimental studies about straw torrefaction

Studies	Experimental equipment	Input (straw)	Nitrogen flow (mL/min)	Heating rate (°C/min)	Torrefaction temperatures (°C)	Residence time (min)
Ferro et al. [2]	Cylindrical reactor	65 g	83.33	N.A	230	60
					250	120
					280	180
Bridgeman et al. [4]	TGA analyzer	25–35 mg	50	10	250	30
					270	
					290	
Wang et al. [3]	Fixed bed reactor	22 g	500	30	200	30
					250	
					300	
Lanzetta and Di Blasi [7]	TGA analyzer	10 mg	N.A	25–70	200–300*	20–50
Prins et al. [8]	Fixed bed reactor	10 g	N.A	10–20	250	30
Sadaka et al. [9]	Muffle furnace	50 g	N.A	N.A	200	15
					260	30
					315	45
						60
						120
						180

* examined range: 127–375 °C

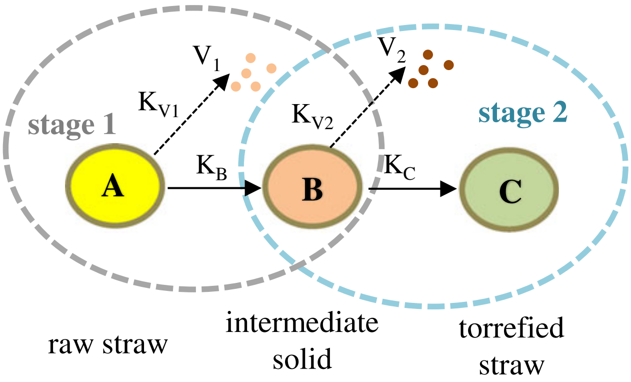

Fig. 1 Two-stage mechanism of torrefaction

For each rate, an Arrhenius type temperature dependency is considered:

$$K_i = k_{0,i} \cdot e^{-\frac{E_i}{RT}}, \quad i = A,\ B,\ C,\ V_1,\ V_2 \tag{3}$$

For a torrefaction operating temperature below 250 °C only the first stage takes place. For temperature higher than 250 °C, there is a specific time, denoted as critical time t*, at which the first stage ends and the second stage begins. This value is important in order to define the evaluation of the process for a certain reaction time, as the kinetic rates representing the torrefaction process change significantly. t* can be calculated analytically taking into account that at this time instant the yield of the intermediate solid B maximizes, according to the following formula:

$$\begin{aligned}\frac{dM_B}{dt} &= K_B M_A - K_2 M_B = 0 \Rightarrow K_B M_0\left(1 - e^{-K_1 t^*}\right)\\ &= K_2 \frac{K_B M_0}{K_1 - K_2}\left(e^{-K_2 t^*} - e^{-K_1 t^*}\right) \Rightarrow t^* = \frac{\ln\left(\frac{K_1}{K_2}\right)}{K_1 - K_2}\end{aligned} \tag{4a}$$

At this time instant t*, the product yield of solid B is denoted as M_B^*. Moreover it stands that:

$$\frac{M_B^*}{M_0} = \frac{M_{V2\infty}}{M_0} + \frac{M_{C\infty}}{M_0} = 1 - \frac{M_{V1\infty}}{M_0} \tag{4b}$$

where $\frac{M_{V1\infty}}{M_0}$, $\frac{M_{V2\infty}}{M_0}$ are the maximum dimensionless (with the initial biomass mass), amount of released volatiles during stages 1 and 2 correspondingly. M_C is the solid residual mass after the end of the devolatilization phase. For straw pellets, based on the literature data from [8], the following expressions were built so that the mass ratios of products C and volatiles V_2 respect to the initial mass M_o $\frac{M_{C\infty}}{M_0}$ and $\frac{M_{V2\infty}}{M_0}$ are calculated as a function of temperature:

$$\frac{M_{C\infty}}{M_0} = 0.60 - 0.0041 \cdot (T[^\circ\mathrm{C}] - 200) = \frac{K_C K_B}{K_1 K_2} \tag{5a}$$

$$\frac{M_{V2\infty}}{M_0} = 0.17 + 0.001 \cdot (T[^\circ\mathrm{C}] - 260) = \frac{K_{V2} K_B}{K_1 - K_2} \tag{5b}$$

$$\textit{and} \quad \frac{M_{V1\infty}}{M_0} = \frac{K_{V1}}{K_1} \tag{5c}$$

According to [1] and [2] the solid residual mass *W* at each time step is given by:

$$\frac{W}{M_0} = \frac{M_A + M_B + M_c}{M_0} = \frac{M_B^*}{M_0} - \left(\frac{M_B^*}{M_0} - \frac{M_{C\infty}}{M_0}\right)\left(1 - e^{-K_2(t-t^*)}\right), \quad t > t_{heat} \tag{6}$$

In these equations the time t is measured from the time that torrefaction begins.

Mass M_A has been determined from the former stage, and M_{V2} is calculated by:

$$\frac{M_{V2}}{M_0} = \frac{M_B^* + M_A - W}{M_0} \Rightarrow \frac{M_{V2}}{M_B^*} = 1 + \frac{M_A - W}{M_B^*} \tag{7a}$$

The reduction of solid M_B due to the reactions at stage 2 is:

$$\frac{dM_B^{B\to C}}{dt} = -K_2 M_B^{B\to C} \Rightarrow M_B^{B\to C} = M_B^*\left(1 - e^{-K_2(t-t^*)}\right) \Rightarrow \frac{M_B^{B\to C}}{M_B^*} = 1 - e^{-K_2(t-t^*)}, \quad t > t_{heat} \tag{7b}$$

where $M_B^{B\to C}$ is the mass of M_B during the second reaction. Hence, the final solid char mass M_C production is easily obtained by:

$$\frac{dM_C}{dt} = -K_C M_B^{B\to C} \Rightarrow \frac{M_C}{M_0} = K_{C\infty}\left(1 - e^{-K_2(t-t^*)}\right) \Rightarrow \frac{M_C}{M_B^*} = \frac{K_C K_B}{K_2(K_1 - K_{V1})}\left(1 - e^{-K_2(t-t^*)}\right), \quad t > t_{heat} \tag{7c}$$

Solid and Gas Products Composition

The proximate (VM (volatiles matter), FC (fixed carbon)) and ultimate (C, H, O) composition of the torrefied biomass can be determined by corresponding arithmetic expressions that are yielded based on data from experimental campaigns of wheat straw torrefaction found in the literature. As far as sulfur content prediction is concerned, there is no data in literature related to the fate of S after the torrefaction process. This is attributed to both the difficulty for accurate S measurement and the low industrial interest about it. Hence, it is made the rough assumption that the whole sulfur remains at the solid biomass. Regarding the nitrogen fate included within the biomass particles, according to the recent study of Medic et al. [14] this is assumed to mainly remain within the solid biomass. Nevertheless, the nitrogen content in the torrefied fuel is so small, that has little effect on the mass and energy balance of the process. Moreover, the initial ash content in terms of absolute mass (kg) still remains in the solid char residue, after torrefaction. This is a reasonable consideration since any mechanism transferring ash from solid to gas phase is not taking place during torrefaction.

For the solid product composition (C, H, O analysis), the arithmetic expressions built-up and used, are based on the experimental data, derived by the work performed by Ferro [2]. In this study, several experimental series are conducted in a lab scale unit using straw pellets as a fuel. The temperature and residence time for which these equations are regarded as valid are 230–280 °C and 0–3 h, respectively.

$$\frac{C_{solid}}{C_{raw}}[\mathrm{kg/kg}] = -0.0014 \cdot T[^\circ\mathrm{C}] - 0.010 \cdot \frac{t[\mathrm{s}]}{3600} + 1.22, \quad t > t_{heat} \tag{8}$$

$$\frac{H_{solid}}{H_{raw}}[\mathrm{kg/kg}] = -0.0040 \cdot T[^\circ\mathrm{C}] - 0.020 \cdot \frac{t[\mathrm{s}]}{3600} + 1.87, \quad t > t_{heat} \tag{9}$$

$$\frac{O_{solid}}{O_{raw}}[\mathrm{kg/kg}] = -0.0050 \cdot T[^\circ\mathrm{C}] - 0.015 \cdot \frac{t[\mathrm{s}]}{3600} + 2.02, \quad t > t_{heat} \tag{10}$$

On the other hand, fixed carbon (FC) and volatiles mater (VM) are dependent on the torrefaction temperature according to the following equations. These equations have been derived from relevant experimental measurements conducted by Bridgeman et al. [3]. In this study, the proximate analysis of torrefied wheat straw was performed for a temperature range of 200–300 °C.

$$\frac{FC_{solid}}{FC_{raw}}[\mathrm{kg/kg}] = -0.0003 \cdot T^2[^\circ\mathrm{C}] + 0.1762 \cdot T[^\circ\mathrm{C}] - 24.149 \tag{11}$$

$$\frac{VM_{solid}}{VM_{raw}}[\mathrm{kg/kg}] = -0.0122 \cdot T[^\circ\mathrm{C}] + 3.88 \tag{12}$$

As aforementioned, the volatiles species are divided into two categories, (a) liquefied at low temperatures named as condensable and (b) non-condensable. According to the literature, the main components of the condensable volatiles part (‘liquid’), derived by wheat straw torrefaction are acetic acid (CH_3COOH) and water (H_2O) [3, 5, 9]. Apart of them, formic acid ($HCOOH$), methanol (CH_3OH), lactic acid ($C_3H_6O_3$), furfural ($C_5H_4O_2$) and hydroxy acetone are also detected [3]. For the reasons of model simplicity, acetic acid and water are assumed as the only condensable components in this study. The produced water originates from the moisture of the initial fuel. The assumption to consider only two condensable species in the products is not expected to influence the accuracy of the mass and energy balance because of the small percentage of liquid yields produced during this mild pyrolysis process [5].

On the other hand, the vast majority of non-condensable components ('gas') are carbon dioxide (CO_2) and carbon monoxide (CO) [3, 5, 9]. The quantity of produced methane (CH_4) can be neglected, without a significant error, since its contribution to the calorific value of the gaseous product is very small [2, 9]. Ferro et al. [2] showed that the CO_2/CO ratio is not highly affected by the residence time; the opposite stands for temperature. The arithmetic expression, which the experimental data [2] can fit onto and is incorporated in the thermodynamic model is given by Eq. 13:

$$\frac{CO_2}{CO} = 0.0004 \cdot T^2 - 0.22 \cdot T + 32.5 \left(\frac{\text{kmol}}{\text{kmol}}\right) \tag{13}$$

The fraction of gas to liquid components is determined based on the relevant studies of Bridgeman et al. [3], Wang et al. [5] and Prins et al. [9]. Fuel origin plays an important role on this ratio, as the devolatilization is strongly affected by the decomposition mechanism and rate of the hemicellulose structure. For instance, Prins et al. [9] detected that the composition and quantity of non-condensable volatile yields, for willow and straw are similar, in contrast to larch. This is attributed to the presence of xylan. Ferro et al. [2] measured a small amount gas content (volatiles), the results of whom are in disagreement with the results of Prins et al. [9]. Based on the literature data [2], we made the rough assumption that the gas to liquid mass ratio is equal to 0.25.

Concerning the heating value, this gets higher as the torrefaction temperature and the residence time increase. For the calculation of the calorific value of the product solid yield the following equation, [2] is used:

$$\text{HHV}_{daf} = 0.34\%\text{C} + 1.40\%\text{H} - 0.16\%\text{O (MJ/kg)} \tag{14}$$

Description of the ASPEN Plus Process Model

For the simulation of torrefaction process, very few process tools are available in the literature, [11, 12]. The thermodynamic tool, describing the straw pellets torrefaction is based on the afore-described modeling approach, integrated in the commercial accredited commercial software ASPEN Plus. The ASPEN Plus flowsheet is depicted in Fig. 2. Torrefaction process is modeled to being performed in two stages as aforementioned, while the equations described in the previous paragraphs, simulate the governing physical mechanisms taking place during this complicated process. In the thermodynamic setup algorithm, reactors type of stoichiometric (RSTOIC) for the two stages are applied.

The feedstock biomass enters the first reactor (RSTOIC) named as 'STAGE1', where the first stage reactions taking place are simulated. Similarly, the reactions taking place during the 2nd stage are conducted in the second RSTOIC named as 'STAGE2'.

Both V_1 and B are defined in the process tool, as non-conventional components, the properties of which (Ultimate, Proximate analysis and Calorific Values) are estimated by the previously described arithmetic expressions The synthesis of composition of outlet streams is done at the RYIELDS 'TORSYN' for solid biomass and 'VOLSYN' for volatiles.

Data for the oil thermophysical properties come from AB&CO [15], and the correlation of each property is extracted (T in °C):

$$C_p = 4.5426 \cdot T + 1864.6 \ [\text{J/kg} \cdot \text{K}] \tag{15}$$

$$\lambda = -7 \cdot 10^{-5} \cdot T + 0.1356 \ [\text{W/m} \cdot \text{K}] \tag{16}$$

$$\rho = -0.8096 \cdot T + 902.24 \ [\text{kg/m}^3] \tag{17}$$

The present model focuses on the calculation of the mass and energy balance of the torrefaction system. In this light, a detailed analysis of heat transfer mechanism within the mass of each particle is not included, as a more rigorous modeling of the reactor would be then required. The only assumption related to the heat transfer mechanism within the particles is related to the temperature difference (25 °C) between the temperature of the heat/cooling medium (i.e. hot oil, cooling water, respectively) and the corresponding temperature of particles at each stage of the reactor. The particles are considered to exhibit a uniform temperature profile, by the adopted approach.

Operation Principles of the Torrefaction Reactor

A schematic view, representing the operation principles of the reactor is shown in Fig. 3. This is a Hearth type reactor.

Operating Conditions

The overall torrefaction process can be sub-divided into two main steps, (a) torrefaction and (b) solids cooling. The medium, which provides the biomass with the required heat, is considered to be hot mineral oil, previously heated up in a furnace. It is assumed that the inlet temperature of the hot oil is 350 °C and its corresponding outlet temperature 15 °C higher than the operating torrefaction temperature, in the reactor. The maintenance of the inert atmosphere inside the reactor is accomplished by injecting pure nitrogen, which is preheated at the torrefaction temperature before it enters the reactor. The required nitrogen flow rate is calculated based on previous studies of torrefaction process at experimental devices [2], where for 65 g

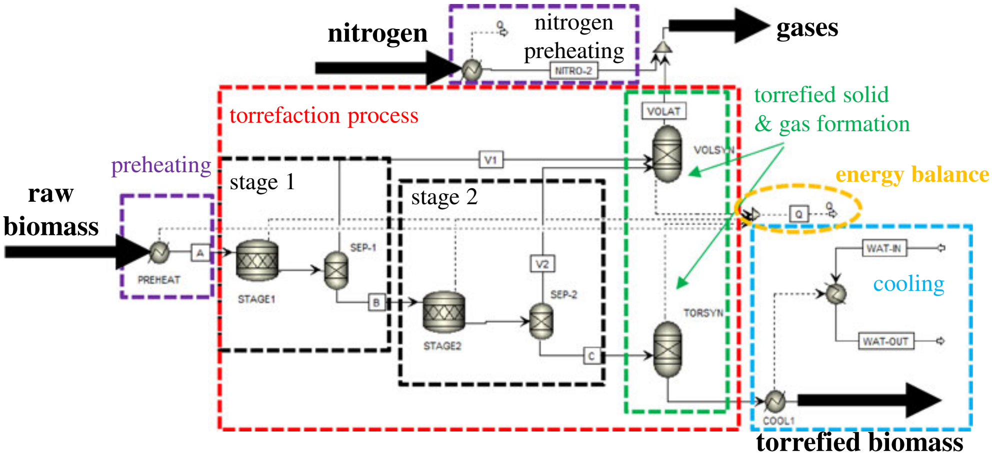

Fig. 2 ASPEN Plus Process flowsheet

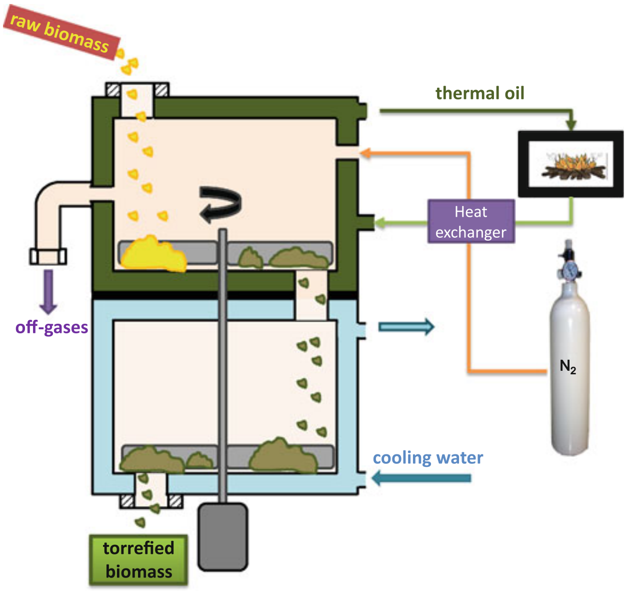

Fig. 3 Schematic representation of the torrefaction pilot plant

of biomass 5 l/h of nitrogen are used. For pilot plants, such data could not be found.

In the second step, the torrefied product is further cooled down below 200 °C, until it reaches the desired final temperature of around 50 °C. The cooling medium is water. The water inlet temperature is set to around 15 °C, while its outlet to 28 °C. The latter value was chosen to be below the value of 50 °C, in order to conform with relevant environmental legislations for an open waste water discharge open circuit.

Pilot Plant Components

The biomass enters the treatment vessel through an upper inlet. Within the vessel, the biomass is subjected to torrefaction and latter is discharged. The biomass is fed continuously from the upper surface of the torrefaction reactor vessel. In its inlet, a chute is applied. This receives the biomass from the inlet and directs it to the trailing section portion of the upper tray. The chute ensures that biomass entering the vessel is retained on the upper tray for nearly a full rotational period of the tray.

The reactor's trays (plates) are circular discs having a generally planar upper support surface. The trays include an opening similar to a pie shaped open section of a circular disc. For each tray there is one circular area, which allows biomass on the upper surface of the tray, to fall through towards the underlying one. The open sections of each tray are not vertically aligned with the corresponding ones in the trays immediately above and below it. This is designed in such a way, so that the required residence time of the biomass at each stage is achieved. The trays are stationary and mounted to the sidewall of the vessel, while an impeller rotates with the shaft and the upper surface of each tray.

The scraper bars may be solid rods, frames with supporting ribs or other radially extending rigid or semi-rigid arm. As the scrapper bars rotate with the shaft, the bars sweep the biomass over the surface of the stationary trays. As the biomass slides over the trays, the biomass is dried and heated by the hot inert gas circulating inside the vessel. For inert gas injection one or more gas inlets are designed. Finally, there may be one or more scraper bars arranged in the radial array for each tray.

Results and Discussion

Model Validation

The model is valid up to a temperature equal to 300 °C. Above this limit, not a mild pyrolysis process takes place and any rates and products compositions calculations based on the equations described in this paper cannot be regarded as valid. As it is discussed in the previous section, all calculations described in this paper are based on experimental data found in literature for wheat straw exclusively. Nevertheless, the described modeling approach can be modified and applied for any solid biogenic fuel based on adequate experimental data for reaction rates and composition yields.

For the validation of the thermodynamic tool, the TGA experimental data presented by Prins et al. [12], are used as a reference. Prins et al. present data for the wheat straw pellets mass reduction rate for two temperatures (248 and 267 °C), the digitizing of which allows for the extrapolation of the kinetic parameters, which describe the mass temporal decrease, during torrefaction. These data are given in Table 2.

The numerical results along with the corresponding experimental data are presented in Fig. 4, depicting a very good agreement for both temperatures.

It should be noted that the model is not capable of providing valid results for lower than 240 °C temperatures, as the experimental data used as an input in the model, do not allow for a torrefaction process to take place for lower than this temperature value.

In the following paragraphs, a parametric study on the implementation of either one single and/or a two batch pilot plant reactor is presented. The developed and validated process tool is capable of giving important information, which can be used for the design and manufacturing of a torrefaction plant, including the effect of:

- HHV (high heating value) of the solid product;
- liquid, gas and solid composition;
- flow rates of the heating (oil), inert gas (nitrogen) and cooling (water) mediums;
- residence time and torrefaction temperature on the torrefaction process overall.

The input data used for the calculations are the raw material characteristics and its feeding flow rate, while the output is the characteristics both of the produced torrefied biomass and the composition of volatiles V2.

Table 2 Kinetic parameters

i	k_0 (s^{-1})	E (J/mol)
B	0.00327	3,485.6
V_1	5×10^{19}	240,657
1	0.1656	20,376
C	0.01921	1.5894×10^4
V_2	84.79	5.629×10^4
2	0.5135	28,692

In the following Figures, we define as heating time (t_{heat}) ($0 < t < t_{heat}$), the time needed for the biomass particles to reach the torrefaction temperature, T_{tor}, and as reaction time the residence time of the particles beyond it. It is assumed t_{heat} to be equal to around 1,500 s according to the kinetics data, we used for this study [16]. This value may vary from case to case, depending on the heating rate, the size of the reactor and the thermochemical properties of the biomass (ρ, C_p, e.t.c). Moreover, during the temperature increase from ambient temperature up to the torrefaction one, devolatilization of biomass is not considered to take place. This assumption is close to reality, since during this period, only internal heating of biomass takes place. Considering biomass evaporation above the temperature of 100 °C, drying of biomass takes place in reality, but this is considered to be included in the first step of the process and represented by the corresponding arithmetic expressions as a function of time. These data are provided by conducting TGA analysis, while the preheating time required to reach the operating torrefaction temperature starting from the ambient one (20 °C) is included.

One Batch Reactor-Solid Product Composition

Table 3 presents the fuel composition of the torrefied biomass (at time t = 3,500 s), as a function of the operating temperature. Since during torrefaction a devolatilization

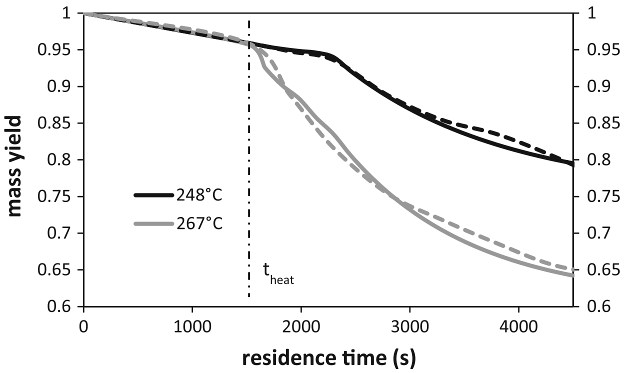

Fig. 4 Model prediction of solid mass yield in comparison with the experimental results (with *dash lines*)

Table 3 Fuel analysis dependence on temperature, t = 3,500 s

T (°C)	Proximate analysis (% w/w dry-basis)			Ultimate analysis (% w/w dry-ash free basis)			
	FC	VM	ASH	C	H	O	N
25 (raw)	19.3	69.6	11.1	49.04	5.72	44.67	0.56
240	17.66	70.50	11.84	50.66	6.00	42.69	0.64
260	30.68	56.55	12.77	52.92	5.90	40.39	0.78
280	42.59	42.69	14.71	55.47	5.77	37.63	1.13

step is conducted, the volatiles mass production is increasing with temperature. In addition, among the three most important substances of the fuel (C, H, O), oxygen is released with the highest rate, thus resulting in higher HHV. Finally, the increase in the ash content should be as well pointed out.

Figure 5 presents the H/C to O/C ratio for the torrefied biomass, reflecting the fact that the torrefied biomass properties resemble more the properties of conventional fuels (coal, lignite) than standard biogenic fuels, thus contributing significantly to the more efficient co-firing concepts of torrefied biomass with conventional fuels, when compared to the raw biomass co-firing.

Furthermore, Fig. 5 provides with extra information about the beneficiary role of torrefaction on the improvement of calorific value of the solid biomass (RS: Raw Straw, TS: Torrefied Straw). Low O/C ratios imply high calorific value (HHV), whereas low H/C ratios imply low LHV. As the temperature increases, more Oxygen is released through devolatilization. On the other hand the Hydrogen content for the raw biomass remains practically constant.

Table 4 gives the molar composition of the released volatiles. The increase of temperature beneficiates the increase of gas heating value (Fig. 6). This is owed to the increase of its combustible content (CO and acetic acid).

One Batch Reactor-Data Performance of the Process

The basic design parameters including the flow rates of the basic streams for the torrefaction pilot plant are presented in Table 5.

From Table 5, it is evident that as the torrefaction temperature is increasing, the required flow rate of the heating medium (thermal oil) is increasing, especially in the range of temperature values more than 250 °C. For a temperature increase of 10 °C, the required flow rate almost doubles. On the other hand, the corresponding cooling water flow rate decreases as less torrefied biomass needs to be cooled down to a temperature equal to around to 50 °C.

In addition, the energy content of the torrefied biomass is increasing with temperature, Fig. 6. For temperatures above 240 °C the HHV of solid upgrades up to 20 %, when compared to the raw material corresponding one. Similar to Ferro et al. [2] study, the parametric study on the reaction time last, for residence times higher than 3,660 s, has not an impact on the achieved calorific value of the solid yield.

The effect of temperature on the temporal evolution of the torrefied mass is depicted in Fig. 7. As the temperature increases, larger portion of the hemicellulose content reacts. For a temperature above 250 °C, where lignin decomposition happens, the mass yield curves are more abrupt. According to this graph, torrefaction temperatures higher than 260 °C should be avoided owed to the very low mass yield earned. This temperature limitation presents a bottleneck for the straw torrefaction as a process, at least for the case of straw pellets. Nevertheless, if the operator's intention is to increase the heating value of torrefied biomass as much as possible, without paying an attention on the increase of energy recovery (ER), higher temperatures than 350 °C are preferable.

Figure 8 depicts the temporal evolution of energy recovery (ER) based on Eq. 18, in dry-ash free basis or different operating temperatures. Values above 100 % at the beginning of the process are valid without violation of

Table 4 Dependence of gas analysis on temperature (% v/v-N_2 free), t = 3,500 s

T (°C)	CO_2 (%)	CO (%)	H_2O (%)	CH_3COOH (%)
240	8.13	3.00	85.34	3.71
260	7.78	3.30	85.22	3.69
280	7.75	3.42	85.18	3.65

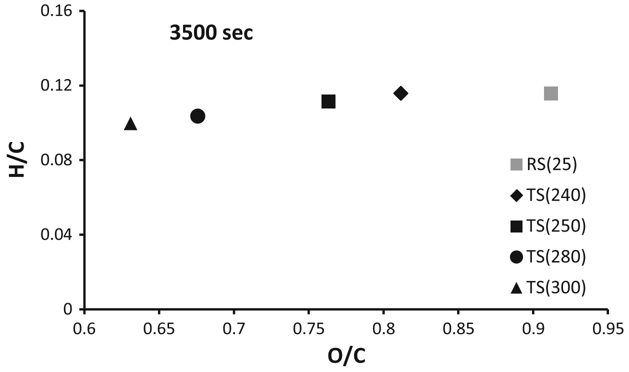

Fig. 5 O/C and H/C ratio at solid samples (RS: raw straw, TS: torrefied straw), at the time instant of t = 3,500 s

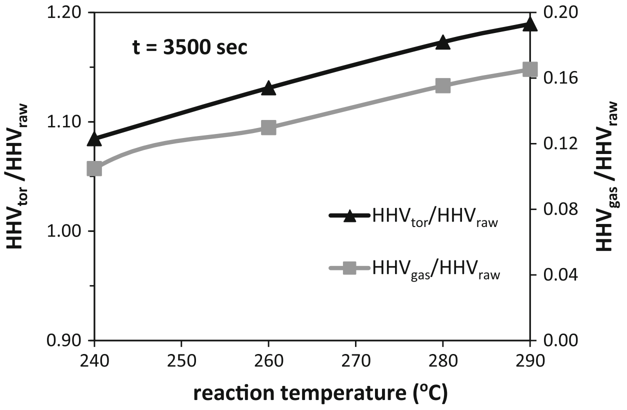

Fig. 6 Upgrade of biomass Calorific Value (HHV), for different Torrefaction temperatures at the time instant of 3,500 s

energy balance, because of the heat input at the system, which is used for the energy upgrade of the fuel and is reflected to the increase of the Heating value of the biomass. However for residence time higher than 1 h, ER converges to an almost constant value. This value is always decreasing with the increase of operating torrefaction temperature.

$$ER = \frac{\dot{m}_{tor} \cdot LHV_{tor}}{\dot{m}_{raw} \cdot LHV_{raw}}, \ \dot{m}_{i(raw,tor)}, \ LHV_{i(raw,tor)} \text{ in daf} \qquad (18)$$

To summarize, based on Figs. 6, 7 and 8 results, one should design a pilot plant operating at temperatures around to 240 °C, for a the highest energy yield to be achieved. This is owed to the fact that the decreasing ratio of mass is higher than the corresponding increasing ratio of the Heating value at quite high temperatures (above 250 °C). This time period allows as well for the operator to get a homogenized torrefied biomass product.

Two Batch Reactor—Solid Product Composition

Except for the standard case of a single batch reactor, a two batch one was as well investigated. In this two-batch reactor, the torrefaction process is conducted in two stages with different operation temperature and residence time. In the first stage, the straw pellets undergo torrefaction up to a certain point, before they re-enter into the second stage, until the torrefaction is completed. In the end an additional stage exists for solids cooling. A schematic view of the apparatus is depicted in Fig. 9.

The process is simulated applying the same methodology. Nevertheless it is made the assumption that the reaction rates at temperatures T_1 and T_2 for torrefied biomass is calculated from the same kinetic model independently the state of the fuel at the beginning of the process (i.e. at the 1st batch the initial fuel is raw whereas at the next batch the initial fuel has already been torrefied up to a point). The corresponding time for the biomass to reach the temperature defined at the second stage (T_2) t_{heat2} has been calculated as being proportional to t_{heat}, starting from the corresponding of the first stage (T_1).

For all cases examined, with parameters being the two operating torrefaction temperatures (one for each stage) and the corresponding residence time, the total residence time is taken equal to around 5,100 s (reaction time of around 1 h). This reaction time lies in between the reported reaction time of biomass during torrefaction, based on various experiments conducted for torrefaction process in the literature [2, 3, 5, 6]. Moreover, this time is considered as enough for the particles to undergo torrefaction, increase their heating value without a significant loss of mass yield.

In order to investigate the effectiveness of a two-batch reactor, a parametric study regarding the effect of temperature and residence time on the operation of the two-batch reactor is conducted. For all cases examined, the residence time, the biomass particles remain at each of the two steps reactor, is the same and equal to the half of the total one. Table 6 presents the final process results of the four scenarios examined.

According to the results of the parametric study, a double-batch reactor with a higher operating temperature at its first stage (scenario 2) has considerable advantages

Table 5 Stream flow rates, required for the torrefied biomass to have the properties as presented in Table 3 at t = 3,500 s

Mass rate (kg/h)	T = 240 °C	T = 250 °C	T = 260 °C
Thermal oil	288	628	1,200
Cooling water	436.8	410.0	376.6
Nitrogen make-up	7.7	7.7	7.7
Solid yield	86.71	80.18	72.27

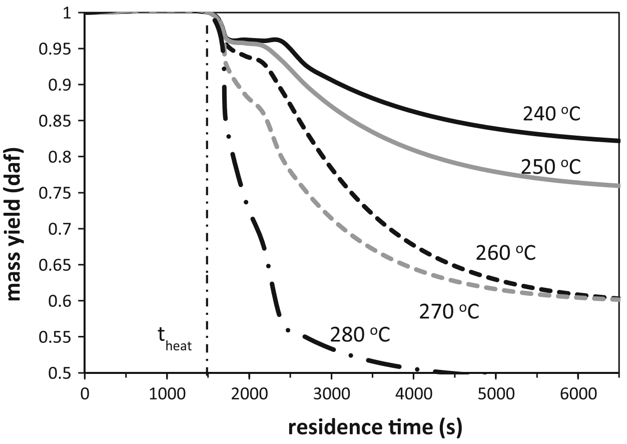

Fig. 7 Temporal evolution of mass yield of torrefied Biomass for different Torrefaction Temperatures

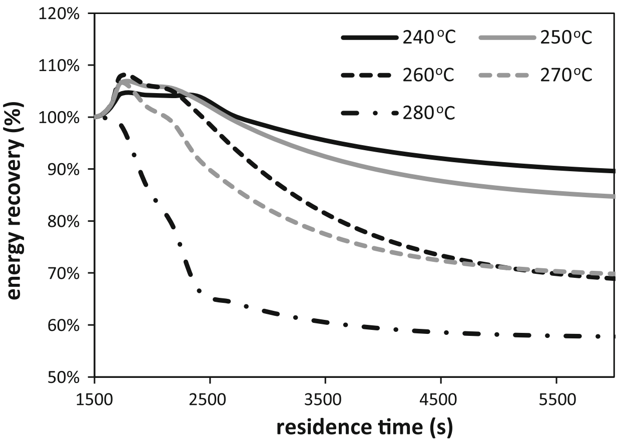

Fig. 8 Temporal evolution of energy recovery (*ER*) of torrefied biomass as a function of Temperature

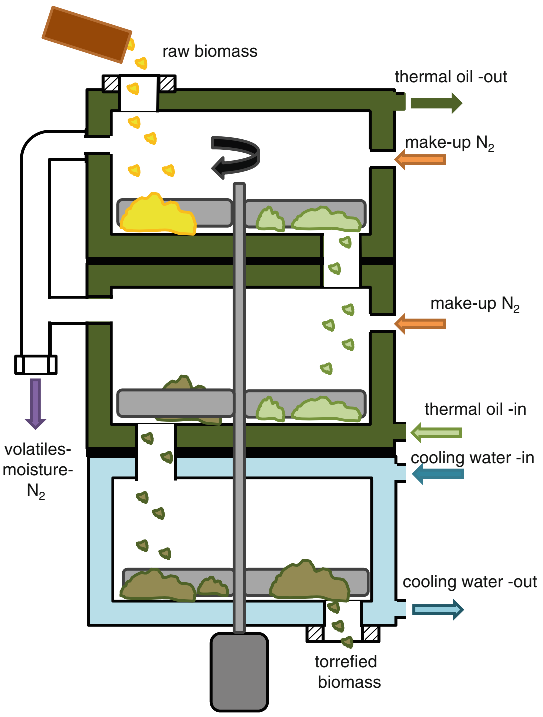

Fig. 9 Schematic representation of two-batch torrefaction reactor

Table 6 Comparison of single-batch and double-batch reactor effectiveness

	Scenario 1	Scenario 2	Scenario 3	Scenario 4
T batch 1 (°C)	240	260	240	260
T batch 2 (°C)	260	240	260	
t_{heat} (s)	1,500	1,500	1,500	1,500
t_1 (s)	1,800	1,800	1,800	3,600
t_2 (s)	1,800	1,800	1,600	
Mass yield (daf %)	68.11 %	77.62 %	69.15 %	72.09 %
HHV_{tor}/HHV_{raw}	1.19	1.19	1.19	1.13
ER (%)	81.20 %	92.53 %	82.43 %	81.62 %

(higher mass yield and energy efficiency) over the single one, as presented in the previous paragraphs (scenario 4). Moreover, the application of a higher temperature at the first stage compared to the second one, favors the efficiency increase, as derived from the comparison of scenario 2 with scenario 1 and scenario 3. Additionally, an equivalent time distribution (scenario 1) between the two stages has not a significant effect on the operation efficiency of the plant, when the time difference is not very high (less than 10 %—scenario 3), in terms of efficiency.

From these results, it is deduced that the division of the process in two steps has a beneficial effect in terms of ER, only if the second batch is operating at a smaller temperature than the first one. Figure 10 depicts the mass loss temporal evolution for each scenario. To conclude, the major advantage of following two stages torrefaction process compared to one stage is that one can achieve higher energy recovery (92 % compared to 81 %) while on the other hand, one has to build a more complex and thus more expensive apparatus for this to be achieved. Specific values cannot be given as we have not made any Cost Benefit Analysis so far.

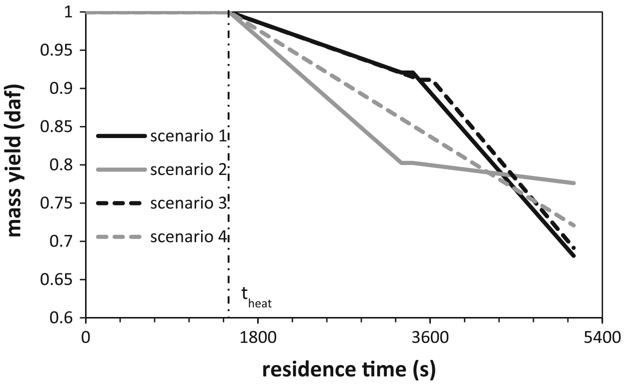

Fig. 10 Mass yield along the reaction time for each scenario

Conclusions

In this study, a process model capable of predicting the values of temperature and residence times, for the most efficient operation of a straw pellets pilot torrefaction plant is described. This model is developed in the commercial software ASPEN Plus®. The model predicts the gas/solid products composition and the rate of biomass mass loss during the process, while the simulation results agree quite well with corresponding experimental data. This model is applied for a straw pellets pilot scale torrefaction reactor and the flow rates of the inert and cooling medium streams are reported. Several preliminary design parameters (number of stages, torrefaction temperature and residence time) are parametrically investigated, allowing for the selection of the most optimal one to achieve maximum efficiency. Within these parameters, the application of a two batch reactor seems to be more preferable than a single one, always under specified conditions and for the case of straw pellets. The composition of the torrefied biomass confirms the beneficiary effect of torrefaction process, for the energy upgrade of the fuel. The comparison of simulation results between one and a two batch reactor reveals that a two-batch reactor can be more efficient than a single one.

References

1. Chew, J.J., Doshi, V.: Recent advances in biomass pretreatment-Torrefaction fundamentals and technology. Renew. Sust. Energy Rev. **15**, 4212–4222 (2011)
2. Ferro, D.T., Vigouroux, V., Grimm, A., Zanzi, R.: Torrefaction of agricultural and forest residues. Cubasolar April 12–16 Guantánamo; Cuba (2004)
3. Bridgeman, T.G., Jones, J.M., Shield, I., Williams, P.T.: Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel **87**, 844–856 (2008)
4. Jaya S. Tumuluru, S. Sokhansanj, Christopher T. Wright, J. Richard Hess, Richard D.: Boardman, A review on biomass torrefaction process and product properties, symposium on thermochemical conversion, Oklahoma State University, Stillwater, OK, August 2011
5. Wang, G., Luo, Y., Deng, J., Kuang, J., Zhang, Y.: Pretreatment of biomass by torrefaction. Chin. Sci. Bull. **56**, 1442–1448 (2011)
6. Shang, L., Ahrenfeldt, J., Holm, J.K., Sanadi, A.R., Barsberg, S., Thomsen, T., Stelte, W., Henriksen, U.B.: Changes of chemical and mechanical behavior of torrefied wheat straw. Biomass Bioenergy **40**, 63–70 (2012)
7. Peng, Y., Wu, S.: The structural and thermal characteristics of wheat straw hemicellulose. J. Anal. Appl. Pyrol. **88**, 134–139 (2010)
8. Lanzetta, M., Di Blasi, C.: Pyrolysis kinetics of wheat and corn straw. J. Anal. Appl. Pyrol. **44**, 181–192 (1998)
9. Prins, M., Ptasinski, K., Janssen, F.: Torrefaction of wood Part 2. Analysis of products. J. Anal. Appl. Pyrol. **77**, 35–40 (2006)
10. Sadaka, S., Negi, S.: Improvements of Biomass physical & chemical characteristics via torrefaction process Environ. Prog. Sustain. Energy **28**(3), 427–434 (2009)
11. Dudgeon, R.: An aspen plus model of biomass torrefaction. University Turbine Systems Research (UTSR) Fellowship (2009)
12. Hardianto, T.H., Pasek, A. D., Suwono, A., Azhari, R., Ardiansyah, W.: The Aspen Simulation of a Peat Torrefaction System. Proceedings of International Symposium on Sustainable Energy and Environmental Protection (ISSEEP) (2009)
13. Di Blasi, C., Lanzetta, M.: Intrinsic kinetics of isothermal xylan degradation in inert atmosphere. J. Anal. Appl. Pyrol. **40–41**, 287–303 (1997)
14. Medic, D.: Darr. M., Shah A., Potter B. Zimmerman J. Effects of torrefaction process parameters on biomass feedstock upgrading. Fuel **91**, 147–154 (2012)
15. http://www.abco.dk
16. Prins, M., Ptasinski, K., Janssen, F.: Torrefaction of wood Part 1. Weight loss kinetics. J. Anal. Appl. Pyrol. **77**, 28–34 (2006)